



## Catalytic ozonation—Effect of carbon contaminants on the process of ozone decomposition

Jacek Nawrocki<sup>1</sup>, Lilla Fijołek\*

A. Mickiewicz University, Faculty of Chemistry, Laboratory of Water Treatment Technology, 89b Umultowska Street, 61-114 Poznań, Poland



### ARTICLE INFO

#### Article history:

Received 4 March 2013

Received in revised form 22 April 2013

Accepted 9 May 2013

Available online 21 May 2013

#### Keywords:

Carbon

Contaminants

Ozone decomposition

### ABSTRACT

Decomposition of ozone into hydroxyl radicals is one of the most frequently discussed hypotheses of the heterogeneous catalytic ozonation mechanism. Estimation of catalytic activity of solid catalysts in the reaction requires the reference system (without the catalyst) with the same pH in which spontaneous ozone decomposition will occur. However, the contaminants of many ozonation catalysts may significantly influence the process of ozone decomposition just by changing pH of water. In this paper the effect of active carbon contaminants on the process of ozone decomposition is discussed. Contaminants are mainly of alkaline character and moreover are easily dissolving in water or acids. Thus the lack of precise control of pH leads to an observation of false catalytic effects connected with the change of pH after the catalyst introduction into the aqueous ozone solution. To differentiate between the effects caused by increased pH and true catalytic activity of potential catalysts strict control of pH is advised. This paper shows that requirement of the same pH in the catalytic and reference system is not as simple as thought before. The observation of the contaminants effects on the process of ozone decomposition explains at least some controversial literature results.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

In the recent years, numerous publications on catalytic ozonation have appeared [1,2]. However, many of the results they have presented are considered controversial [1,2]. In general catalytic ozonation is often classified as an advanced oxidation process in which the generation of hydroxyl radicals is the main feature. Thus the heterogeneous catalysts are expected to decompose ozone into radicals in the much more intense way than the generation of the species by spontaneous ozone decomposition. Catalytic ozonation is expected even to generate hydroxyl radicals at low pHs [1,2]. In such a process, precise control of pH is necessary in order to differentiate between the effects caused by unexpected pH changes and catalytic activity of potential catalysts. Active carbons, including commercially available ones, have been widely investigated as catalysts in the process of ozonation, both as unmodified materials [3–5] and as carriers [6,7]. Activated carbon does not act as a catalyst but rather as an initiator and/or promoter of ozone transformation into •OH radicals, because its textural and especially chemical properties are modified during ozonation treatment. The role of a promoter/initiator of chain reactions, has been demonstrated in

papers [3,8,10]. Even small amounts of carbon may enhance ozone decomposition, even in the presence of decomposition process inhibitor [8,9]. In supporting information (SI), a number of papers are listed (Table S1), in which commercially available active carbons were used as catalysts decomposing ozone. The mechanism of ozone decomposition has been investigated in three different systems: (i) without pH control, (ii) with pH adjustment with acids, (iii) with the buffers of very wide range of concentrations (5–100 mM) (see Table S1). Moreover a very wide range of catalyst concentrations (from 0.1 g/L to 40 g/L) have been used for estimation of the catalytic effects. Commercially available active carbons are always contaminated with ash. Elemental composition of ash in a number of active carbons has been analyzed by Rivera-Utrilla and Sanchez-Polo [3]. The analysis revealed that the main elements detected in ash are silicon, aluminum and iron. Apart from that, the ash contained large amounts of Mg and Ca. Literature, however, lacks information on the solubility of mineral components of active carbon contaminants. Only in a few papers, active carbons were purified by demineralization for the analysis of their catalytic activity [3]. The solubility of the contaminants is a crucial information from the catalytic ozonation view point. The alkaline character of the contaminants will tend to change pH of the ozonated water to higher values and that would obviously influence the ozone decomposition.

Therefore the main aims of this paper are as follows: (i) analysis of elemental composition of soluble contaminants of active carbons, (ii) estimation to what extend the contaminants may

\* Corresponding author.

E-mail addresses: [jaceknaw@amu.edu.pl](mailto:jaceknaw@amu.edu.pl) (J. Nawrocki), [lilla@amu.edu.pl](mailto:lilla@amu.edu.pl) (L. Fijołek).

<sup>1</sup> Tel.: +48 61 829 1582.

influence the pH of ozonated waters and (iii) an estimation of the effects of the contaminants on ozone decomposition, (iv) showing how important the strict control of pH is in catalytic ozonation, particularly when commercial materials of unknown purity are used.

## 2. Experimental

### 2.1. Materials and analytical methodology

Seven commercially available carbons have been used: Filtrasorb 400 (F400-Chemviron Carbon), Filtrasorb 300 (F300-Chemviron Carbon), GAC 830W (830W-Norit), GAC 830Supra (830S-Norit), DGF AX 8 × 30/65 (DGF AX-Carbotech AC) Aquasorb 6300 8 × 30 (Aquasorb-Jacobi Carbons), Silcarbon S1020 (Silcarbon-Silcarbon Activkhole). Carbons were sieved and the most abundant fractions were selected for experiments (0.5–1.5 mm or 1.5–3.15 mm). Carbons were purified by HCl extraction (19% azeotropic aqueous solution) for 5 h followed by an extraction with high purity water (Millipore) for another 5 h in an apparatus similar to one described in paper [13]. Both extracts were combined and subjected to elemental analysis using ICP-OES (Varian ICP-OES Vista-MPX). HCl was selected for carbon extraction as a strong non-oxidizing acid which does not cause structural changes and changes in oxygen content of functional groups in carbon [14].

Ozone in gas phase was determined using the iodometric method, while ozone dissolved in water was determined with indigo method; both methods have been described in Standard Methods [15].

The pH<sub>pzc</sub> value was determined using slightly modified method suggested by Faria et al. [11]. The amounts of electrolyte and carbon were doubled, while pH was equilibrated for 24 h [12].

### 2.2. Ozone decomposition

Experiments of ozone decomposition in water were conducted at room temperature, in high purity unbuffered water (Millipore), whose pH was corrected to pH 2.5 or pH 5.0 with hydrochloric acid (3.45 mM/L HCl and 2.02 μM/L HCl, respectively). Before each series of experiments, in order to ensure zero ozone demand, the reactor was saturated with ozone for 20 min. In each experiment 200 ml highly pure water, with appropriate pH, was introduced to 250 ml glass reactor. Ozone was produced from pure oxygen using the Crystal ozonator (Canada). Water was saturated with ozone for 20 min, after that time the concentration of ozone in the water phase was approximately  $4.77 \pm 0.51$  mgO<sub>3</sub>/L. After switching off the ozonator, a zero sample was immediately taken and 0.5 g of appropriate carbon was introduced. Ozone concentration was measured at specified time intervals. Similar experiments were also done for aqueous solutions of ozone buffered with 0.005 and 0.010 M phosphate buffers.

## 3. Results and discussion

### 3.1. Composition of commercially available active carbons

In order to identify contaminants in carbon samples, qualitative and quantitative analysis of extracts obtained in the process of carbon purification was conducted. The results are presented in Table 1.

As shown in Table 1, over twenty different metals were found in the extracts, including large quantities of alkaline elements.

In total, active carbons may contain metallic contaminants ranging from 90 to almost 700 μmol/g. Three different groups of carbons can be distinguished: (1) with multivalent metals (Fe, Al, Si, and Ti) prevailing over alkaline metals (Li, Na, K, Mg, Ca), this

group includes carbons F-300, F-400 and GAC 830W; (2) with alkaline contaminants occurring in amounts similar to multivalent elements contaminants (DGF AX and Aquasorb), and (3) with prevailing alkaline elements (GAC 830S and Silcarbon).

Generally, the analysis of extractable elements confirms the results obtained by Rivera-Utrilla and Sanchez-Polo [3] for ashes from active carbons. Ash analysis indicated the prevailing (among contaminants) role of silicon. In extracts, much more significant role is played by alkaline elements (Mg, Ca and Na, K an even Sr and Li). Moreover, Al, Fe and Ti have been found. It is obvious that alkaline metals frequently occurring in carbons will be largely responsible for changes in water pH during its contact with carbon. No direct relationship can be found between the effect caused by carbons on water pH and the amount of contaminants. In many papers (see Table S1), the pH of the determined solution is corrected using acid, and only afterward active carbon (catalyst) is introduced. The lack of further pH control (following the introduction of carbon during and after the process) seems to be a serious experimental error in view of the data below. Alkaline contamination of carbons to a great extent affects the pH of ozonated water, which in turn influences the rate of ozone decomposition. Therefore, one may suspect that the observed decomposition of ozone is caused not only by the activity of carbon surface but also by significant pH changes.

### 3.2. Stability of pH after introduction of carbon catalysts to water

Catalytic ozonation must be conducted at known and controlled pH, with the reference solution i.e. water (with the same pH). In many papers (Table S1), buffers are used to control pH, but in many others the pH value is obtained by adjustment with acid or alkali. Controlling pH using a buffer ensures constant pH reaction, but only in case when possible contaminants do not exceed the buffer capacity. In a great majority of papers, the solution pH is not controlled after the introduction of carbon as catalyst, which usually results in the risk of significant pH change.

Catalytic activity of a catalyst in the reaction of ozone decomposition may be determined only in comparison with a reference system at the same pH. Usually water or buffer at required pH is ozonated and the spontaneous decomposition of ozone is observed. In the next step the same volume of water or buffer (at the same pH) is ozonated again and the catalyst is introduced and again the decay of ozone is observed. The problem arises when the introduction of the catalyst changes pH of ozone solution. Adjustment of the pH value of ultrapure water (Millipore) with hydrochloric acid is commonly used in catalytic ozonation: the correction to pH 5 requires very little amount of acid (about 10 μmol/L). Correction to pH 2.5 requires larger amounts of acid (about 3.45 mmol/L). The required pH may be of course obtained with buffers. Do we stabilize pH with such methods when active carbons are used as catalysts? We have performed all the experiments with acid adjusted and buffer adjusted pHs and with using purified and unpurified active carbons. After 30 min of ozone decays pHs of the catalyzed ozone solutions differed very much from those of the reference solutions. The results are in Table 2.

What is seen from the results of Table 2 is inappropriate pH stabilization of all acid adjusted solutions when unpurified active carbons were used as catalysts. Using of non-extracted active carbon (0.5 g/200 mL) may increase pH by 4 units particularly when pH close to neutrality are investigated. Extracted carbons give negligible pH increases for acidic solutions (at pH 2.5) but at pH 5 we observed pH increases of about 0.2–0.3 pH units. The surprising results have been obtained with buffers at pH 5. The 0.01 mM phosphate buffer does not stabilize pH at pH 5 and the observed differences between catalyzed and reference solutions are even higher than for unbuffered solutions. What are the reasons for the

**Table 1**

Quantitative and qualitative composition of extracts obtained after purification of carbons. The result is the sum of acid and water extracts.

| Chemical element         | F300 ( $\mu\text{mol/g}$ ) | F400 ( $\mu\text{mol/g}$ ) | DGF AX ( $\mu\text{mol/g}$ ) | GAC 830W ( $\mu\text{mol/g}$ ) | GAC 830S ( $\mu\text{mol/g}$ ) | Silcarbon ( $\mu\text{mol/g}$ ) | Aquasorb ( $\mu\text{mol/g}$ ) |
|--------------------------|----------------------------|----------------------------|------------------------------|--------------------------------|--------------------------------|---------------------------------|--------------------------------|
| Al                       | 84.93                      | 87.70                      | 172.15                       | 201.57                         | 1.84                           | 0.86                            | 162.58                         |
| B                        | 2.94                       | 3.24                       | 0.52                         | 2.44                           | 1.90                           | 1.14                            | 14.55                          |
| Ca                       | 43.90                      | 47.60                      | 182.30                       | 50.28                          | 27.76                          | 15.51                           | 98.44                          |
| Co                       | 0.12                       | 0                          | 0.15                         | 0.10                           | 0                              | 0                               | 0.07                           |
| Cr                       | 0.08                       | 0.10                       | 0.09                         | 0.12                           | 0                              | 0                               | 0.12                           |
| Cu                       | 0.14                       | 0.17                       | 0.04                         | 0.04                           | 0.09                           | 0.07                            | 0.04                           |
| Fe                       | 70.38                      | 70.39                      | 118.51                       | 76.35                          | 1.32                           | 0.85                            | 71.95                          |
| K                        | 7.82                       | 8.88                       | 7.31                         | 4.52                           | 25.90                          | 206.75                          | 49.42                          |
| Li                       | 1.05                       | 0.86                       | 0.62                         | 0.57                           | 0                              | 0                               | 0.23                           |
| Mg                       | 11.53                      | 12.07                      | 101.77                       | 15.26                          | 11.59                          | 13.52                           | 43.62                          |
| Mn                       | 0.48                       | 0.48                       | 0.96                         | 0.99                           | 0.24                           | 0.06                            | 0.34                           |
| Na                       | 8.40                       | 9.01                       | 30.42                        | 12.27                          | 7.74                           | 31.60                           | 10.63                          |
| Ni                       | 0.12                       | 0                          | 0.07                         | 0.25                           | 0.01                           | 0                               | 0.11                           |
| P                        | 3.40                       | 3.64                       | 2.41                         | 15.16                          | 5.52                           | 9.32                            | 4.50                           |
| S                        | 8.87                       | 8.60                       | 10.71                        | 4.16                           | 0.55                           | 0.63                            | 2.81                           |
| Si                       | 30.66                      | 40.86                      | 58.08                        | 26.51                          | 8.67                           | 9.79                            | 31.02                          |
| Sr                       | 1.46                       | 1.34                       | 1.76                         | 1.69                           | 0.18                           | 0.20                            | 4.22                           |
| Ti                       | 8.80                       | 9.99                       | 4.76                         | 6.03                           | 0.04                           | 0.02                            | 8.69                           |
| V                        | 0.39                       | 0.50                       | 0.15                         | 0.48                           | 0                              | 0                               | 0.27                           |
| Zn                       | 0.01                       | 0.01                       | 0.06                         | 0.08                           | 0.02                           | 0.02                            | 0.04                           |
| Total                    | 305.44                     | 285.48                     | 692.84                       | 418.87                         | 93.37                          | 290.34                          | 503.65                         |
| Total: Al, Fe, Ti, Si    | 187.43                     | 208.94                     | 353.5                        | 309.19                         | 11.87                          | 11.52                           | 274.24                         |
| Total: Ca, Na, K, Li, Mg | 72.7                       | 78.42                      | 322.42                       | 82.9                           | 72.99                          | 267.38                          | 202.34                         |

observed phenomena? For acid adjusted solutions and the unpurified carbons the amount of acid at pH 5 is insufficient to compensate alkalinity of metals dissolving from carbons. Higher amount of acid used for adjustment to pH 2.5 allows to get relatively stable pH conditions when 0.5 g/200 mL are used. But in many papers (Table S1) much higher concentrations of carbon catalyst were used in catalytic ozonation research.

It is clear that highly pure water normally used in experiments which confirm the catalytic activity of carbon, does not have buffer capacity and it is susceptible to pH changes caused by inorganic contaminants. The greatest pH changes observed after the introduction to water at pH 5 are caused by relatively pure carbons GAC 830S and Silcarbon. The changes reach over 4 pH units. Silcarbon contains relatively large amounts of potassium, sodium, calcium and magnesium, and those alkaline metals seem to be responsible for the observed pH increase. GAC 830S contains smaller quantities of potassium, but similar contents of Na, Ca and Mg. The common feature of these two carbons is relatively low content of Al, Fe and Si. Carbon GDF AX, which contains very high content of contaminants, including substantial amounts of Ca and Mg, does not cause such significant pH changes, probably due to the high concentrations of Al, Fe and Si (which absorb the alkalinity).

Similar conclusions can be drawn observing the influence of Aquasorb on water pH. Therefore, it may be assumed that the content of aluminum, iron and silicon will reduce the influence of alkaline metals on pH of water suspensions of commercial carbons. As could be expected, extracted carbons influence water pH corrected to pH 5 to a lesser extent, and to a minimal extent – water at pH 2.5. That indicates that mineral contaminants of carbons are responsible for those changes. Similar phenomena were observed

by Faria [7] during the ozonation of pigments using cerium oxide supported on carbon.

Even slight changes in solution pH may suggest the participation of contaminants in the process of ozonation. The observation is crucial as the changes in solution pH in the process of catalytic ozonation have been either omitted or not measured at all (Table S1).

Substantial changes in water pH may be expected near the neutral pH, following the introduction of not only non-extracted commercial carbons, but also purified carbons. As shown in the results (Table 2), pH correction using acid does not guarantee stable pH during the ozonation of suspension. This should be ensured by controlling pH with buffers.

### 3.3. Do buffers sufficiently control pH?

As mentioned above, phosphate buffers with the concentrations ranging from 5 to 100 mM (Table S1) were used in the previously published papers. Buffer concentration should correspond not only to the amount of catalyst used (as concentrations of active carbons ranged between 0.1 g/L and 40 g/L, Table S1), but also to their purity. Using a buffer to control pH should not therefore entitle to omission of pH measurements during and after the ozonation process. We realize the fact that the process of organic compounds ozonation (catalytic and non-catalytic) may usually lead to lowering the pH due to the production of acidic by-products of ozonation [1,2]. This paper, however, has investigated pH changes during the processes of ozone decomposition and in all cases pH increase was observed. Buffers' capacity can be easily exceeded by alkaline contaminants in commercial carbons. Such a case is presented in Fig. 1, which

**Table 2**

Changes in pH after 30 min following the introduction of carbon to water (0.5 g carbon in 200 mL), initial water pH corrected by HCl, extracted material (E), and phosphate buffer (BF 0.01 M).

|                                     | O <sub>3</sub> | F300 | F400 | DGF AX | 830W | 830S | Silcarbon | Aquasorb |
|-------------------------------------|----------------|------|------|--------|------|------|-----------|----------|
| $\Delta\text{pH } 2.5$              | -0.02          | 0.1  | 0.11 | 0.06   | 0.08 | 0.11 | 0.20      | 0.09     |
| $\Delta\text{pH } 2.5 \text{ E}$    |                | 0.06 | 0.04 | 0.03   | 0.04 | 0.07 | 0.06      | 0.04     |
| $\Delta\text{pH } 2.5 \text{ E-BF}$ | 0              | 0.06 | 0.06 | 0.03   | 0.04 | 0.06 | 0.06      | 0.05     |
| $\Delta\text{pH } 5.0$              | -0.03          | 1.06 | 0.72 | 1.20   | 0.47 | 4.10 | 4.88      | 0.94     |
| $\Delta\text{pH } 5.0 \text{ E}$    |                | 0.25 | 0.12 | -0.04  | 0.26 | 0.25 | 0.17      | 0.19     |
| $\Delta\text{pH } 5.0 \text{ E-BF}$ | -0.01          | 0.49 | 0.36 | 0.24   | 0.27 | 0.38 | 0.44      | 0.3      |

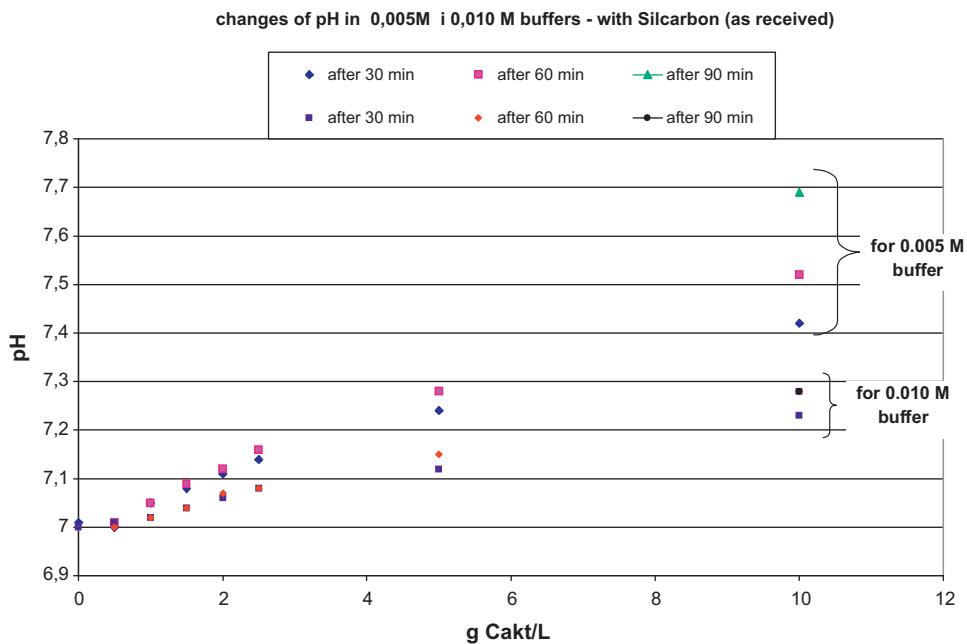


Fig. 1. Changes in pH in 0.005 M and 0.01 M phosphate buffers with increasing amounts of Silcarbon.

illustrates pH changes in 0.005 M and 0.010 M phosphate buffers after the introduction of increasing amounts of Silcarbon.

As can be seen, 0.005 M buffer does not ensure sufficient control of pH during the catalytic ozone decomposition experiment. It seems obvious that pH increase during the catalytic experiment causes higher ozone decomposition. In the case of highly alkaline Silcarbon, 0.005 M buffer does not have enough capacity, and even a buffer with twice as large concentration would not sufficiently stabilize pH. (Note, that during ozone decay experiment (no catalyst) the pH does not change). In SI we have also shown that in respect to other contaminated carbons the control of pH with 0.005 M buffers is not effective (see Tables S2 and S3). Fig. 1 also indicates the significant role of time: the pH of solution with exceeded buffer capacity is strongly dependent upon time, which has been especially well illustrated by data concerning 0.005 M buffer with 10 g/L carbon.

The results in Table 2 show that the introduction of purified carbons to 10 mM buffer will not ensure stable pH. To explain this we analyzed the buffer equilibrated with carbon samples (5 g carbon/100 mL buffer). Adsorption of the buffer on carbons was observed in all cases, which is shown by the decrease of phosphorus concentration in relation to pure buffer. The results of elemental analysis of buffers equilibrated with all carbons are shown in Table 3.

As it follows from Table 3 data, each carbon reacts differently with the phosphate buffer. In some carbons adsorption of phosphates is larger, while in others it is less significant. The changes in phosphates concentration are also accompanied by changes in sodium concentrations and, to a lesser extent, in the silicon concentrations. The highest adsorption of phosphates was observed for

F300 and this is related to the 0.49 pH change. Even after obtaining the evidence for phosphate adsorption on carbon surface, it remains unclear why relatively large pH changes are observed. The above changes suggest the necessity of pH control in all instances when the aim of the study is an explanation of catalytic ozonation mechanisms. The increase in pH may cause ozone decomposition with the generation of hydroxyl radicals, which may be incorrectly interpreted as a catalytic effect.

The above experiments prove that the application of commercially available materials (or other materials which may be contaminated) for catalytic ozonation requires the detailed control of pH.

It is not only the presence of alkaline metals that poses a threat to the understanding of mechanism of catalytic activity of active carbons. The occurrence of soluble contaminants in commercially available materials tested as possible catalysts in the process of ozonation also raises other doubts – to what extent the process of catalytic activity is caused by the presence of catalyst, and to what extent contaminants are responsible for the process. Many experiments on catalytic ozonation are carried out at decreased pH, one of the important by-products of ozone decomposition may be H<sub>2</sub>O<sub>2</sub> [16]. It is therefore also possible that the presence of Fe may lead to the formation of Fenton system and generation of hydroxyl radicals which do not originate from the carbon used as catalyst.

### 3.4. Extraction of carbon and changes in its properties

Extraction of mineral contaminants of carbons significantly changes their structure: first and foremost the carbon content

Table 3

Changes in elemental composition of phosphate buffer 0.01 M (100 ml + 5 g C) after 48 h equilibration of extracted carbons (in relation to pure buffer).

|            | F300 (E) ( $\mu\text{mol/g}$ ) | F400 (E) ( $\mu\text{mol/g}$ ) | DGF AX (E) ( $\mu\text{mol/g}$ ) | 830W (E) ( $\mu\text{mol/g}$ ) | 830S (E) ( $\mu\text{mol/g}$ ) | Silcarbon (E) ( $\mu\text{mol/g}$ ) | Aquasorb (E) ( $\mu\text{mol/g}$ ) |
|------------|--------------------------------|--------------------------------|----------------------------------|--------------------------------|--------------------------------|-------------------------------------|------------------------------------|
| K          | 0.36                           | 0.36                           | 0.02                             | 0.06                           | 0.02                           | 0.12                                | 0.21                               |
| Mn         | -0.01                          | -0.01                          | 0.00                             | -0.01                          | -0.01                          | -0.01                               | -0.00                              |
| Na         | 7.83                           | -1.74                          | 1.74                             | -2.61                          | -5.22                          | -8.70                               | 0.87                               |
| P          | <b>-54.19</b>                  | <b>-56.13</b>                  | <b>-41.94</b>                    | <b>-60.65</b>                  | <b>-63.87</b>                  | <b>-54.19</b>                       | <b>-53.55</b>                      |
| Si         | 0.94                           | 0.47                           | 4.47                             | 2.00                           | 0.19                           | 0.37                                | 4.33                               |
| <b>ΔpH</b> | <b>0.49</b>                    | <b>0.36</b>                    | <b>0.24</b>                      | <b>0.27</b>                    | <b>0.38</b>                    | <b>0.44</b>                         | <b>0.3</b>                         |

The bold values are used to emphasize adsorption of phosphate buffer on AC.

**Table 4**

Characteristics of studied carbons (E – materials extracted with HCl).

| Carbon        | $S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) | Pore volume ( $\text{cc/g}$ ) | Pore diameter (nm) | % N  | % C   | % H  | % S  |
|---------------|--|-------------------------------|--------------------|------|-------|------|------|
| F300          | 796  | 0.57                          | 2.86               | 0.41 | 87.9  | 0.40 | 0.85 |
| F300 (E)      | 817  | 0.57                          | 2.92               | 0.62 | 90.5  | 0.40 | 0.75 |
| F400          | 785  | 0.58                          | 2.97               | 0.37 | 85.1  | 0.55 | 0.80 |
| F400 (E)      | 785  | 0.57                          | 2.89               | 0.41 | 88.3  | 0.39 | 0.85 |
| DGF AX        | 839  | 0.50                          | 2.39               | 0.36 | 88.8  | 0.55 | 0.36 |
| DGF AX (E)    | 919  | 0.55                          | 2.39               | 0.23 | 92.7  | 0.47 | 0.25 |
| GAC 830S      | 1031                                       | 0.61                          | 2.37               | 0.15 | 95.3  | 0.64 | 0    |
| GAC 830S (E)  | 1002                                       | 0.59                          | 2.37               | 0.20 | 96.6  | 0.64 | 0.14 |
| GAC 830W      | 855  | 0.56                          | 2.62               | 0.30 | 85.7  | 1.42 | 0.46 |
| GAC 830W (E)  | 786  | 0.50                          | 2.56               | 0.43 | 89.5  | 0.49 | 0.54 |
| Silcarbon     | 934  | 0.53                          | 2.27               | 0.20 | 93.2  | 0.83 | 0.09 |
| Silcarbon (E) | 1049                                       | 0.60                          | 2.28               | 0.19 | 96.9  | 0.28 | 0.13 |
| Aquasorb      | 881  | 0.70                          | 3.20               | 0.48 | 88.17 | 0.58 | 0.30 |
| Aquasorb (E)  | 793  | 0.65                          | 3.26               | 0.37 | 88.5  | 0.44 | 0.33 |

**Table 5**Changes in  $\text{pH}_{\text{PZC}}$  caused by extraction of commercial carbons (non-purified, purified carbons (E)).

|                                     | F300 | F400 | DGF AX | 830W | 830S | Silcarbon | Aquasorb |
|-------------------------------------|------|------|--------|------|------|-----------|----------|
| $\text{pH}_{\text{PZC}}$            | 10.0 | 9.9  | 8.0    | 10.0 | 10.9 | 10.3      | 10.3     |
| $\text{pH}_{\text{PZC}} (\text{E})$ | 8.9  | 7.1  | 6.0    | 7.4  | 8.5  | 8.8       | 6.9      |
| $\Delta$                            | 1.1  | 2.8  | 2      | 2.6  | 2.4  | 1.5       | 3.4      |

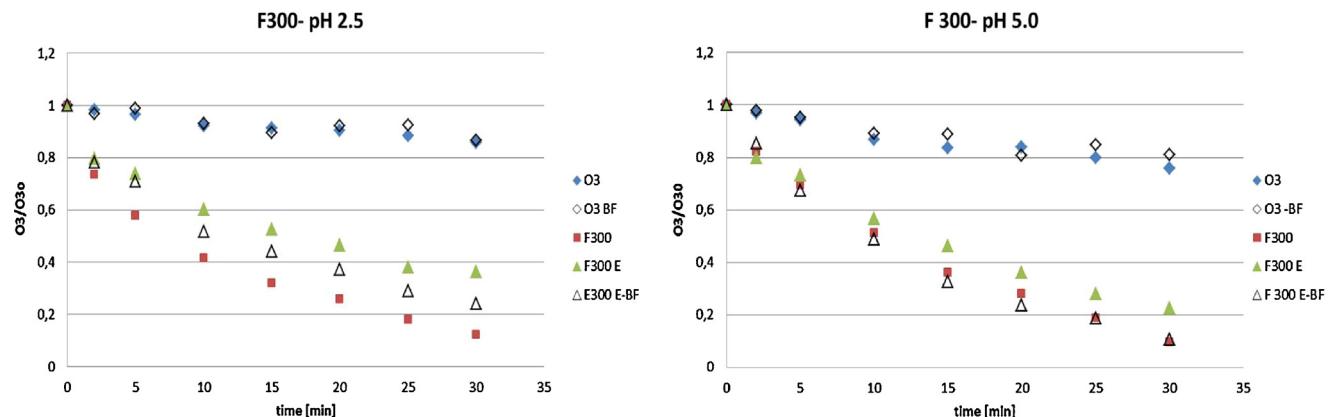


Fig. 2. Decomposition of ozone on F-300, F-300 E (extracted with HCl) at pH 2.5 and pH 5 (corrected with acid) and in 0.010 M phosphate buffer (F-300 E BF).

increases. The carbon content in extracted samples shows also that a part of mineral contaminants is not extracted by hydrochloric acid and remains in the carbons structure. Some publications assume that the difference between 100% and sum of C, H, N and S is caused by the presence of oxygen [3], such a statement, however, seems

to be risky without the analysis of demineralised carbon for the presence of ash.

The highest increase of the carbon content after the extraction was observed for the most contaminated material DGF AX. The extraction of mineral contaminants causes changes in the

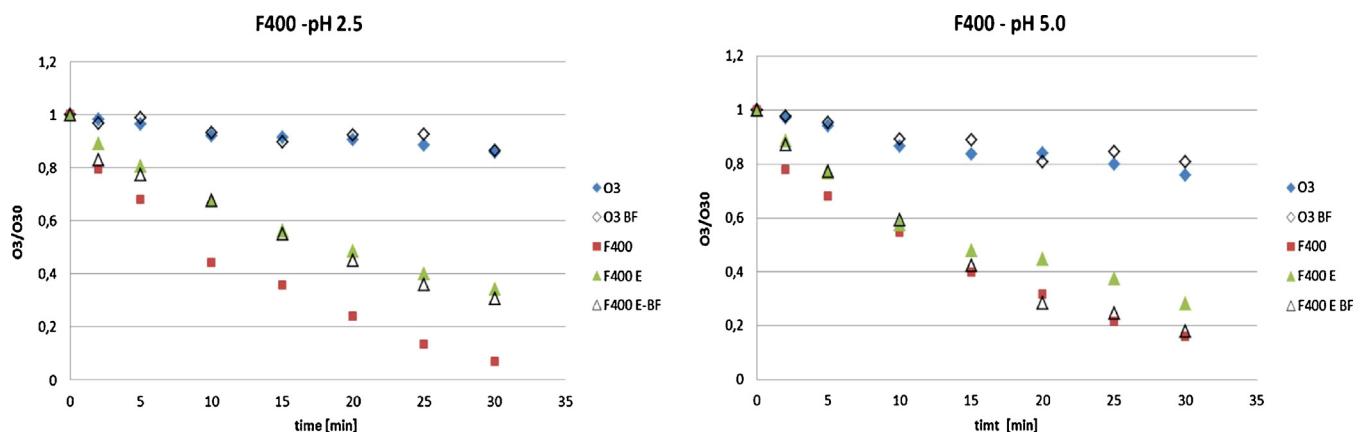
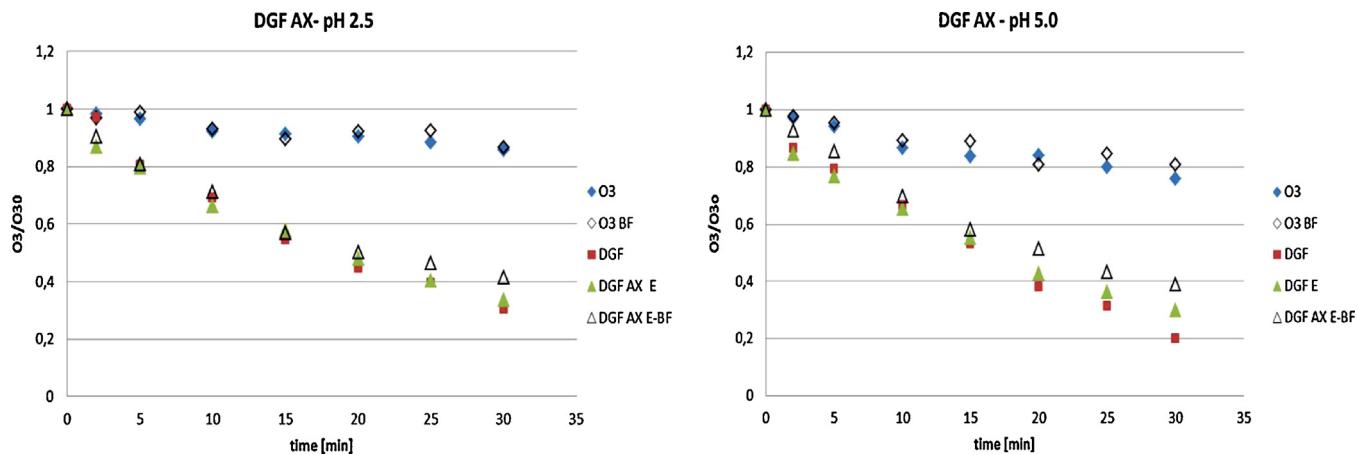
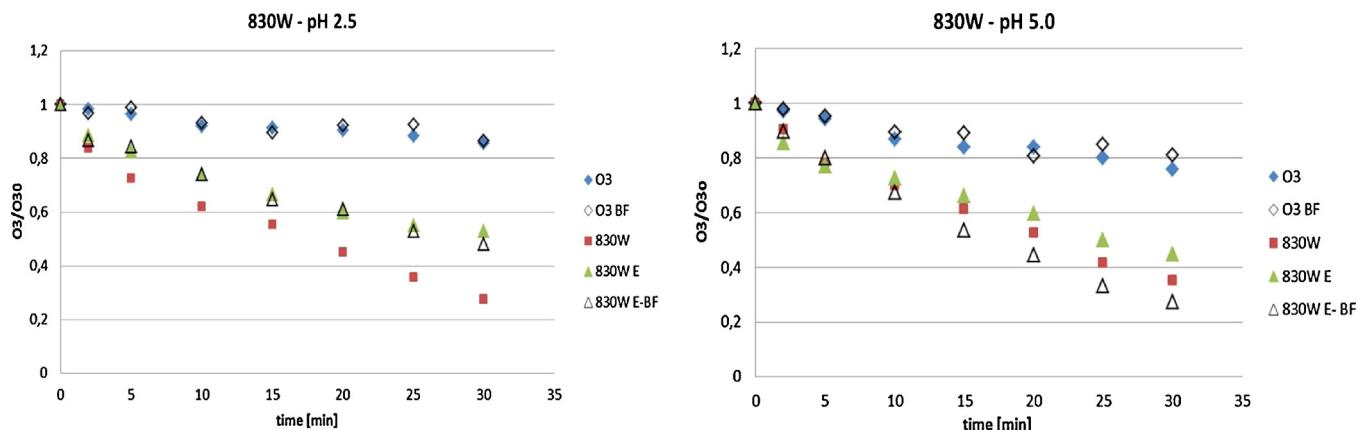


Fig. 3. Decomposition of ozone on F-400, F-400 E (extracted with HCl) in water at pH 2.5 and pH 5 (corrected with acid) and in 0.010 M phosphate buffer (F-400 E BF).



**Fig. 4.** Decomposition of ozone on DGF AX, DGF AX E (extracted with HCl) in water at pH 2.5 and pH 5 (corrected with acid) and in 0.010 M phosphate buffer (DGF AX E BF).



**Fig. 5.** Decomposition of ozone on 830W, 830W E (extracted with HCl) in water at pH 2.5 and pH 5 (corrected with acid) and in 0.010 M phosphate buffer (830W E BF).

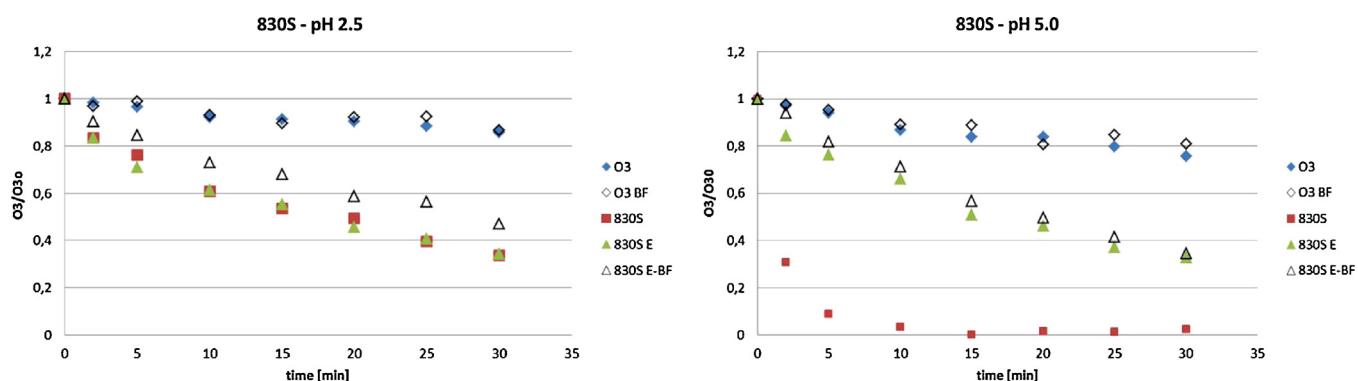
specific surface area, but these changes are not homogeneous; in some cases the area increases, while in others – it slightly decreases.

As results from Table 4, determination of concentration of carbons alkaline surface centers by an acid titration [11,12] of non-purified carbons should be considered incorrect. Extraction of inorganic contaminants from commercial carbons significantly affects their  $pH_{pzc}$ . The values  $pH_{pzc}$  for purified materials are lower

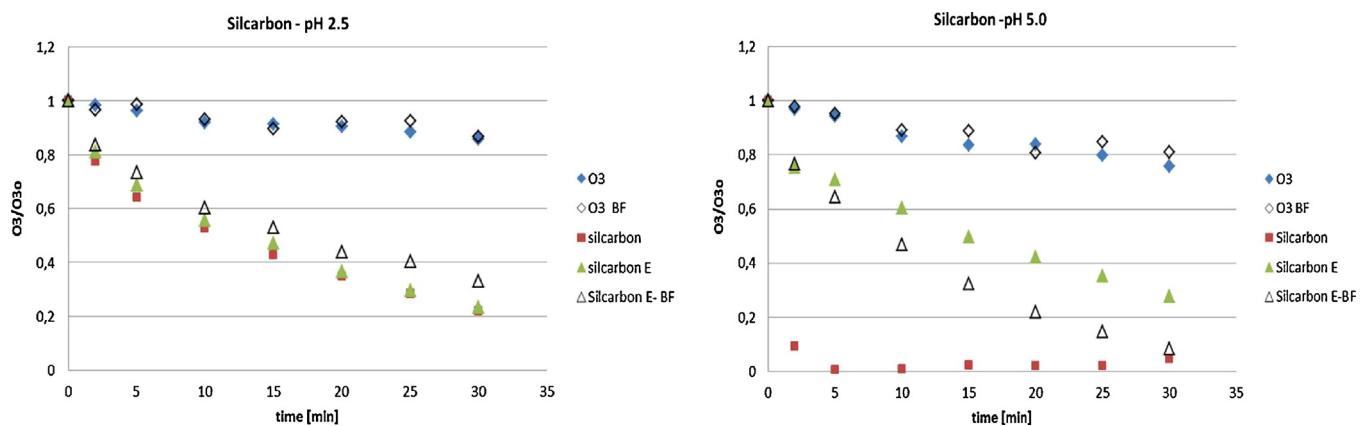
by about 2 pH units than those of “as received” carbons. This is presented in Table 5.

### 3.5. Decomposition of ozone on active carbons

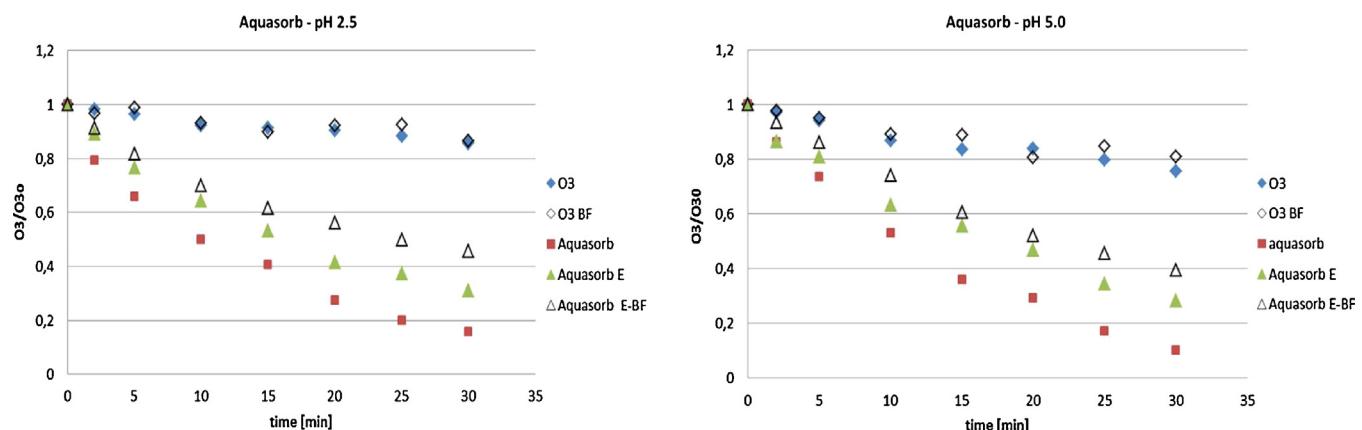
Active carbons are able to decompose ozone, although their true catalytic activity may only be assessed when the pH of reference solution and the pH of carbon suspension are identical. Maintaining



**Fig. 6.** Decomposition of ozone on 830S, 830S E, (extracted with HCl) in water at pH 2.5 and pH 5 (corrected with acid) and in 0.010 M phosphate buffer (830S E BF).



**Fig. 7.** Decomposition of ozone on Silcarbon, Silcarbon E (extracted with HCl) in water at pH 2.5 and pH 5 (corrected with acid) and in 0.010 M phosphate buffer (Silcarbon E-BF).



**Fig. 8.** Decomposition of ozone on Aquasorb, Aquasorb E (extracted with HCl) in water at pH 2.5 and pH 5 (corrected with acid) and in 0.010 M phosphate buffer (Aquasorb E-BF).

identical pH for water and suspension with carbon is easy when very small quantities of catalyst (carbon) are used, but at larger concentrations (g/L) the pH stabilization is not so obvious, even using buffers.

The graphs (Figs. 2–8) clearly indicate the influence of inorganic contaminants on the process of ozone decomposition, which is, however, diversified and depends on the composition of admixtures of particular active carbons. In most cases (at both initial pHs) nonextracted (contaminated) active carbons cause the fastest decomposition of ozone. This can be explained by the highest observed increases of pH (see Table 2). The highest increase of pH (at initial pH 5) is observed for the carbons 830S and Silcarbon that contained particularly high loads of alkali metals. The pH increase significantly influenced the ozone decomposition rate as could be expected. Extraction of the carbons with HCl removes mainly alkali metal contaminants and the materials loose their ability to change the pH of ozone solutions. This results with a similar activity of the carbons toward ozone. Extracted (with HCl) materials (830S and Silcarbon) behave similarly to other extracted carbons. The carbons contaminated with Al, Fe and Si behave differently: they do not increase pH of the solutions so much.

The strongest effects are related to the content of alkaline metals in carbons, whose presence is not “compensated” by the presence of multivalent metals such as Al, Fe, Ti or Si – Gac 830S and Silcarbon. This influence was assessed mainly on the basis of increasing water pH during the introduction of carbon to water. We should, however, bear in mind that a number of metals may be dissolved in acidic

environment and cause additional effects, which are not the subject of this paper.

#### 4. Conclusions

- Observation of catalytic activity of heterogeneous catalysts in the reaction of ozone decomposition requires a reference system at the same pH (without the catalyst) where spontaneous decomposition of ozone occurs
- All materials used as catalysts may be contaminated. Particular attention should be paid to commercially available materials. Such materials are always contaminated and the contaminants may affect the pH of catalyst suspension in water.
- Commercially available active carbons are particularly contaminated with inorganic material. Contamination of active carbons involves large quantities of alkaline elements (Na, K, Mg, Ca) and multivalent elements such as Al, Fe, Si. It seems that these two groups of contaminants can have opposing influence on the pH of carbon suspensions in water. Therefore, purified materials should be used when assessing the catalytic activity of commercially available active carbons.
- The removal of inorganic contaminants of carbons leads to significant changes in surface properties, such as changes in  $\text{pH}_{\text{pzc}}$ , specific surface area and other parameters of carbons porosity.
- The correction of pH using acid or alkali in catalytic ozone decomposition studies is a highly insufficient method for stabilizing the

pH. Using buffers does not entitle to omission of pH control procedures because low concentrated buffers may not stabilize pH sufficiently.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.05.028>.

## References

- [1] J. Nawrocki, B. Kasprzyk-Hordern, *Applied Catalysis B: Environmental* 99 (2010) 27–42.
- [2] J. Nawrocki, L. Fijołek, *Ochrona Środowiska* 31 (3) (2009) 3–16.
- [3] J. Rivera-Utrilla, M. Sanchez-Polo, *Applied Catalysis B: Environmental* 39 (2002) 319–329.
- [4] F.J. Beltran, F.J. Rivas, L.A. Fernandez, P.M. Alvarez, R. Montrelo-de-Espinoza, *Industrial and Engineering Chemistry Research* 41 (2002) 6510–6517.
- [5] F.J. Beltran, B. Acedo, F.J. Rivas, O. Gimeno, *Ozone Science and Engineering* 27 (2005) 159–169.
- [6] J. Ma, M. Sui, T. Zhang, C. Guan, *Water Research* 39 (2005) 779–786.
- [7] P.C.C. Faria, J.J. Orfao, M.F. Pereira, *Applied Catalysis B: Environmental* 88 (2009) 341–350.
- [8] U. Jans, J. Hoigne, *Ozone Science and Engineering* 20 (1) (1998) 67–90.
- [9] M. Guzia, A. Ouederni, A. Ratel, *Ozone Science and Engineering* 26 (2004) 299–307.
- [10] M. Sanchez-Polo, U. von Gunten, J. Rivera-Utrilla, *Water Research* 39 (2005) 3189–3198.
- [11] P.C.C. Faria, J.J.M. Orfao, M.F.R. Pereira, *Water Research* 38 (2004) 2043–2052.
- [12] H. Valdes, M. Sanchez-Polo, J. Rivera-Utrilla, C.A. Zaror, *Langmuir* 18 (2002) 2111–2116.
- [13] W.A. Aue, P.P. Wickramanayake, J. Müller, *Analytica Chimica Acta* 125C (1981) 175–178.
- [14] C. Moreno-Castilla, F. Carrasco-Marin, F.J. Maldonado-Hador, J. Rivera-Utrilla, *Carbon* 36 (1/2) (1998) 145–151.
- [15] Standard Methods for the Examination of Water and Wastewater, 22nd ed., APHA/AWWA/WEF, 2012.
- [16] F.J. Beltran, *Ozone Reaction Kinetics for Water and Wastewater Systems*, Lewis Publishers, 2004.